Kinetics and Mechanisms of Aqueous-Phase Photosensitized Reactions of Imidazole-2-carboxaldehyde and 3,4-Dimethoxybenzaldehyde with α,β-Unsaturated Carbonyl Compounds

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Light-absorbing compounds in the aqueous particulate phase of the atmosphere can act as photosensitizers, initiating photochemical reactions that lead to the formation of secondary organic aerosols (SOA).\textsuperscript{1} Although several studies have been conducted on the formation and aging of SOA, the influence of photosensitizers in the aqueous and particulate phases is far from being fully understood due to the limited availability of kinetic data, product analyses, and mechanisms for photosensitized reactions.\textsuperscript{1,2}

In the present study, we focus on the photosensitized reactions of methyl vinyl ketone (MVK), methacrolein (MACR) and methacrylic acid (MCA) in the aqueous phase through excited imidazole-2-carboxaldehyde (2-IC). The reactions were studied by laser flash excitation-laser long path absorption setup\textsuperscript{1} for the kinetics studies and ultra-performance liquid chromatography coupled with high-resolution electrospray ionization spectrometry for analytical product formation studies. The second-order reaction constants of excited 2-IC with MVK: \( k = (1.0 \pm 0.1) \times 10^9 \) L mol\(^{-1}\) s\(^{-1}\) at pH 4 – 5 and 9, with MACR: \( k = (1.4 \pm 0.4) \times 10^9 \) L mol\(^{-1}\) s\(^{-1}\) and \( k = (1.5 \pm 0.1) \times 10^9 \) L mol\(^{-1}\) s\(^{-1}\) at pH 4 – 5 and 9, and with MCA: \( k = (1.4 \pm 0.4) \times 10^9 \) L mol\(^{-1}\) s\(^{-1}\) and \( k = (1.1 \pm 0.1) \times 10^8 \) L mol\(^{-1}\) s\(^{-1}\) at pH 4 – 5 and 9 were determined. The main products of the Paternò-Büchi reaction, a [2+2]-photoinduced cycloaddition reaction between 2-IC and monomeric and dimeric forms of MVK, were oxabicyclic and dioxabicyclic compounds. Similarly, the addition reactions between 3,4-dimethoxybenzaldehyde (DMB) and MVK were also studied. In case of the excited DMB the second-order reaction constants with MVK: \( k = (1.5 \pm 0.2) \times 10^8 \) L mol\(^{-1}\) s\(^{-1}\) at pH 9, with MACR: \( k = (1.1 \pm 0.1) \times 10^8 \) L mol\(^{-1}\) s\(^{-1}\) and \( k = (2.8 \pm 0.5) \times 10^8 \) L mol\(^{-1}\) s\(^{-1}\) at pH 2 and 9, and with MCA: \( k = (5.2 \pm 1.2) \times 10^6 \) L mol\(^{-1}\) s\(^{-1}\) at pH 9 were obtained. From the product studies, it was found that an addition reaction of excited 2-IC or excited DMB with the unsaturated reactants produces high molecular weight accretion compounds. The data obtained will be used to propose a reaction mechanism to be included in the CAPRAM model to evaluate the influence of these types of photochemical reactions on aerosol oxidative aging and SOA formation.

References
